

Chemical Mapping of the Marine Microlayer: A System for Measurement of Spatial and Temporal Variations in Composition

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LONG-TERM GOALS

The viscoelastic behavior of the air-sea interface, which is an important factor affecting air-sea exchange of mass, momentum and heat, is strongly dependent on naturally-occurring adsorbed surfactant materials (Frew, 1997; Frew and Nelson, 1998). My goals are to understand the relationship between the composition of surface-active organic matter in the marine microlayer and the viscoelasticity of the sea surface and to delineate the role of microlayer films in modulating roughness and near-surface turbulence, and the implications for interpreting both active and passive microwave imagery of the sea surface.

OBJECTIVES

The occurrence, spatial distribution, concentration and composition of sea surface films are not well known. In order to understand the impact of the microlayer on air-sea interactions, it is advantageous to make real-time or near real-time measurements of microlayer concentration and composition using a detection system that responds to a broad range of organic compounds and that also provides specific structural information. This new project focuses on developing an analytical system for detection and measurement of organic analytes in the marine microlayer in near real-time. The system will detect the presence of surface microlayer films, map their spatial distributions, and monitor their temporal variability. It will provide specific information on the composition and structure of surface-active materials and estimates of surface enrichments of specific surfactants that control the viscoelasticity of the sea surface.

APPROACH

A rotating cylinder microlayer skimmer (Carlson *et al.*, 1988) will be coupled with innovative ion trap mass spectrometry technology to map spatial and temporal variations in microlayer film accumulations and their specific composition. An automated sampling interface, intended for deployment on the air-sea interaction catamaran LADAS (Bock *et al.*, 1998) will process the skimmer flow stream, carrying out cyclical, microscale solid-phase extraction, concentration, desalting, and elution of microlayer surface-active organics for short-term archiving in an autosampler-compatible vial array. The time-series 'snapshots' of the extracted microlayer will then be processed by a shipboard ion trap mass spectrometer (ITMS) to develop the surface compositional profile of the area surveyed by the skimmer, with a temporal resolution of a few minutes.

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WORK COMPLETED

Extraction conditions have been studied using model and natural surfactants. Electrospray ionization conditions and instrumental sensitivity limits for model surfactants also have been studied. A paper explaining the instrumental concept and preliminary results was presented at IGARRS99 in Hamburg (Frew and Nelson, 1999).

RESULTS

We have focused on extraction of model and natural surfactants from a seawater matrix using reverse-phase microtraps with bed volumes of 50 μl . Retention and elution efficiencies using the microtraps were found to be strongly dependent on loading conditions. Since the range of compound types and polarities expected for seawater surfactants is large, no single set of conditions was satisfactory for all compound classes. Addition of methanol (2% v/v) to seawater samples prior to loading prevented collapse of the sorbent and elution with methanol provided good recoveries for the widest range of surfactant compounds, including peptides, stanols, stenols, and poloxamers. Complete recovery of fatty acids and derivatives (acyldiglycerides, acyltriglycerides and glycosylglycerides), which bind more strongly to the C-18 sorbent, required a higher percentage of organic additive during loading.

We have used electrospray ionization (ESI) because it appears to be more stable and reliable than chemical ionization over extended periods. ESI of eluates in methanol with 1% acetic acid produced protonated molecular ions for most model compounds of interest; fatty acids were more easily detected in the negative ion mode. ESI-ITMS was used to quantitate concentrations of specific compounds in complex surfactant mixtures by monitoring several sequential stages of ion fragmentation unique to the target compounds. Experiments involving sequential flow injections of microextracts of increasing volumes of Vineyard Sound surface water demonstrated a linear ESI response for both total ion current and specific ion fragmentation pathways for target surfactants in the water. For example, we were able to get a linear ESI-ITMS response for a poloxamer surfactant isolated on the trap for sample sizes down to a few ml. Based on these results, a 10 ml sample size appears to be realistic and, at a 5 ml min^{-1} flow rate, a sample can be loaded onto the trap in only 2 minutes. We have demonstrated the quantitation of a small surface-active tetrapeptide (Met-Arg-Phe-Ala) in seawater using microtrap extraction and ESI-ITMS with virtually no chemical noise. Figure 1 (top panel) shows a full scan ESI mass spectrum of organics isolated from a 5 ml sample of Sargasso Sea water spiked with a low concentration of this peptide. The quantitation of this model compound was accomplished with multistage MS (MS^n) by monitoring the fragmentation pathway: m/z 524 \rightarrow 435 \rightarrow 288. This corresponds to the sequential losses of amino acids phenylalanine and alanine from the C-terminus (Figure 1, middle panel). The extract was flow-injected into the ESI-ITMS, which performed a group of three scan types repetitively during the elution of the sample: a full mass scan (MS^1), a two-stage (MS^2) scan and a three-stage (MS^3) scan. The MS^2 fragmentation pattern is shown in the bottom panel of Figure 1. In this scan, the protonated molecular ion for the target compound (m/z 524) was isolated in the ion trap and then further fragmented by collisional dissociation. The resulting spectrum was free of chemical interference and uniquely identified the compound even though the seawater extract was a complex mixture. System response was linear and could be used to quantify the original concentration of the peptide in the extract.

The results thus far are very encouraging and we are going ahead with the design and construction of a hardware system based on the microtrap concept.

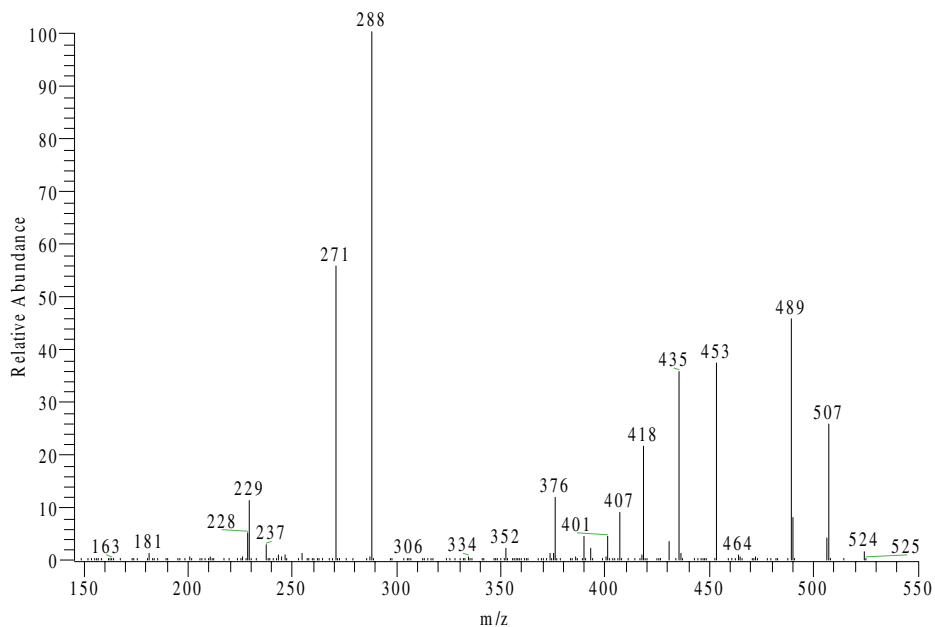
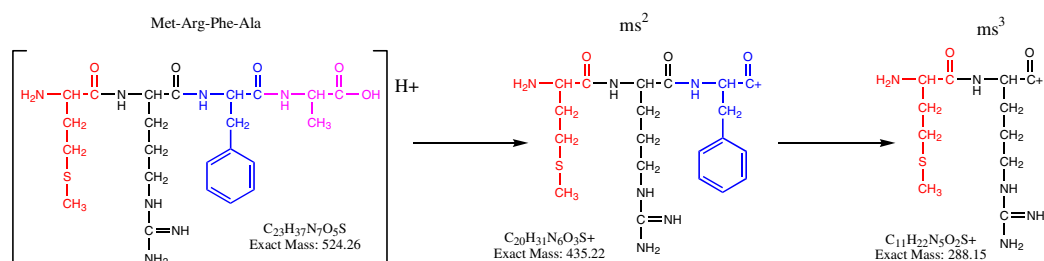
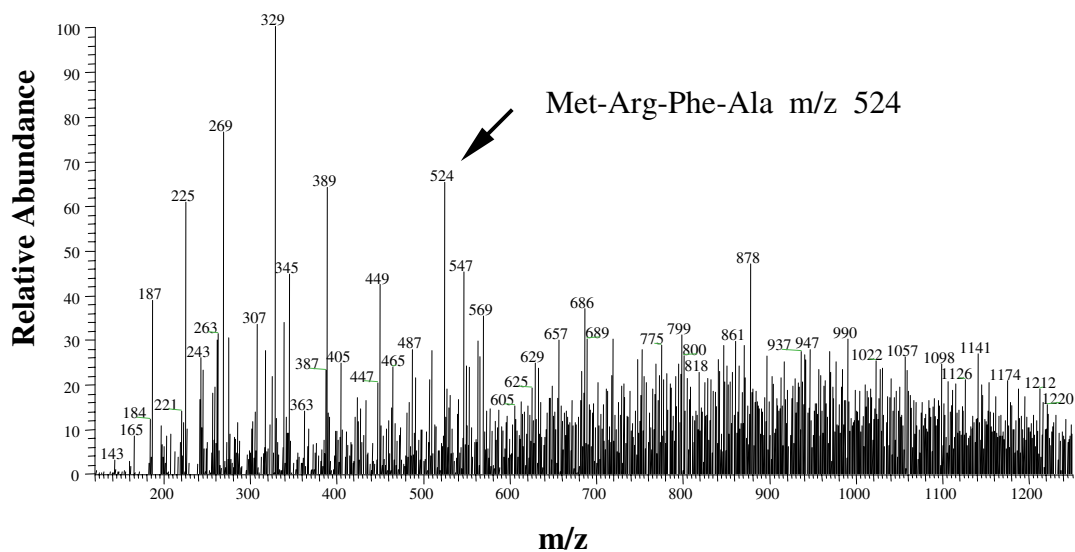


Figure 1. (Upper): Full scan ESI mass spectrum (MS^1) of a Sargasso Sea sample containing a low level spike of the surface-active tetrapeptide (Met-Arg-Phe-Ala). (Middle): Fragmentation pathway of peptide showing sequential amino acid losses. (Lower): MS^2 spectrum of the peptide obtained by isolation of the protonated molecular ion (m/z 524) and subsequent collisional dissociation.

IMPACT/APPLICATIONS

Deployment of the combined sampling package and ion trap mass spectrometer will provide the capability to determine the molecular identity and concentrations of organic compounds in the sea surface microlayer and to make better estimates of surface elasticity. The availability of such information during field studies will allow more detailed investigations of air-sea interactions and improved ground truthing of microwave remote imagery. More rapid information acquisition will allow process studies of links between biology, surfactant production and film distributions, the role of hydrodynamic processes in film formation and dispersal, photochemical degradation processes in the microlayer, and the relative importance of insoluble lipid and soluble biopolymeric surfactants in determining sea surface viscoelasticity. Expected major applications include studies of the role of the marine microlayer in modulating small scale waves and microwave scattering, microwave signatures of internal waves, wind stress-drag relationships, and turbulent surface renewal and air-sea gas exchange.

TRANSITIONS

None as yet.

RELATED PROJECTS

This project is closely related to a NSF Coastal Ocean Processes effort to understand the role of wind stress, small scale waves, near-surface turbulence, and surface films in modulating air-sea gas exchange (with E. Bock, J. Edson, W. McGillis and T. Hara).

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